Enynes connected through aromatic rings are used as substrates for metathesis reactions. The reactivity of three ruthenium carbene complexes is compared. The resulting 1,3-dienes are suitable precursors of polycyclic structures via a Diels–Alder process. Some domino RCM-Diels–Alder reactions are performed, suggesting a possible beneficial effect of the ruthenium catalyst in the cycloaddition process. Other examples require Lewis acid cocatalyst. When applied to aromatic ynamines or enamines, a new synthesis of vinylindoles is achieved. Monitoring of several metathesis reactions with NMR shows the different behavior for ruthenium catalysts. New carbenic species are detected in some reactions with an important dependence on the solvent used.

**Introduction**

Multiple bond metathesis reactions are synthetically useful tools to achieve molecular complexity in an elegant way. Both double-double bond and double-triple bond processes are possible, being the most used intramolecular reactions. The ring-closing alkene-alkyne reaction formally implies the formation of a carbon–carbon bond and the migration of the alkylidene part onto the alkyne carbon, to form a diene, constituting a complete atom economical reaction (Scheme 1). This reaction has been developed later than the diene version. However, in the past 5 years there has been great interest in intramolecular enyne metathesis especially with regard to further transformations of the resulting conjugated dienes. Thus, tandem transformations have led to synthetic applications in the field of polycycle construction and natural product syntheses.

still few data about their practical results, especially in enyne metathesis. There is not a clear rule that indicates the best catalyst to use in each example. Subtle variations in the substrate structure and in the type of final product may lead to different results with each type of carbene complex. In particular, the substitution pattern, the steric demand of the substrate, the ring size to be formed, and the presence of coordinating heteroatoms have important influence on the results.

With regard to the mechanism, the metathesis reaction begins with the dissociative loss of a phosphine and the formation of a 14 e⁻ intermediate (Scheme 2). The formation of this infrequent unsaturated complex was demonstrated with kinetic studies. The increase in the activity of the second generation catalysts is not due to increase in the rate of the phosphine dissociation but to a better ratio of the coordination of the olefin constant (kₚ) and that for the phosphine recovery (k₋). This stage was studied for the alkene-alkene reaction but is shared by the enyne process.

In contrast to diene metathesis there are still some obscure points in the following stages of the enyne reaction. In principle, up to three reaction courses would be possible, depending on the type of coordination of the metal with the system. The metal may coordinate with the double bond (path a, Scheme 3) or with the triple bond with two possible regiochemistries (paths b and c). Hoye has monitored the reaction by NMR and shown the formation of carbene complexes compatible with the first reaction course (path a). Additionally, this path explains better the results obtained in cascade metathesis reactions with dienynes. Nevertheless, with substituted alkynes, Mori has obtained products coming from path c, which implies the initial coordination of the metal with the triple bond. Probably several reaction mechanisms are competing and operate depending on the substrate (steric and electronic effects) and the reaction conditions. In addition, the intermolecular reaction developed more recently after pioneering studies by Blechert is better explained by first coordination of the triple bond with the metal. One possible explanation would be the kinetic versus thermodynamic control of the addition of metal alkylidenes to triple bonds, which might depend on the substitution of the triple bond.

As ring-closing enyne metathesis provides 1,3-dienes, the combination of this reaction with a Diels–Alder cyclization is attractive and allows great increment of the molecular complexity. This approach can be accomplished by addition of all of the reagents from the beginning of the process or by addition of the dienophile when the metathesis is completed. In the first case only electron-deficient dienophiles can be used in order to avoid undesired cross-metathesis reactions. The latter approach has been used for the synthesis of indenes and polycyclic β-lactams. Some examples in which this approach is carried out in a stepwise fashion have also been reported.

In a preliminary communication of this work, we showed the formation of tri- and tetracyclic compounds by the tandem metathesis-Diels–Alder reaction of aromatic enynes. Herein we describe the complete results of our study in which we have compared the reactivity of the different generations of catalysts. We have monitored some reactions by NMR to give some more data on the enyne metathesis reaction course. This methodology is also applied to the synthesis of the indole nucleus.

Results and Discussion

Enynes connected through an aromatic ring are interesting substrates that have found scarce use in this
However, these compounds can be easily prepared and would give, upon metathesis, dienes containing fused bicycles that may undergo a Diels–Alder process to give finally two or three new cycles in one step.

We first carried out the synthesis of 1,6-, 1,7- and 1,8 enynes. Starting from 2-iodobenzyl alcohol, a Sonogashira coupling with trimethylsilylacetylene gave quantitatively alcohol 4, which was oxidized with MnO₂ to give 5 in 99% yield. This aldehyde was treated with suitable Grignard reagents to afford the corresponding enynes 6. Additionally compound 6b was mesylated and treated with superhydride to give 9 (Scheme 4).

To effect a new approach to Dane's diene, a well-known substrate thoroughly used for the synthesis of estradiol derivatives, we carried out the synthesis of the corresponding enyne precursor. Thus, 4-bromo-3-methylanisole was dibromated with NBS to give a dibromide intermediate, which upon basic treatment gave aldehyde 10 in 82% yield after the two steps. Sonogashira coupling afforded 11 quantitatively, which was treated with allylmagnesium bromide to give 12. The final step was the elimination of the hydroxyl group via mesilation-supreydride reduction, yielding 13. We have to note the excellent yield of all steps of this synthesis, the global yield from commercial 4-bromo-3-methylanisole being 68%. The order of the reactions is important. When we tried the Sonogashira coupling with the starting anisole or after treating aldehyde 10 with the Grignard reagent, the yields were much lower (Scheme 5).

2-Iodophenol and 2-iodoaniline were selected as starting materials for the synthesis of enynes containing heteroatoms. These were submitted to Sonogashira coupling conditions to give 14 and 15. Mitsunobu reaction with allyl and homomallyl alcohols afforded enynes 17a,b, whereas 18 was obtained via nucleophilic substitution. Amine 18 was acetylated to give compound 19. The final deprotection of the alkyne yielded the desired enynes 20b, 21a,b, and 22. The synthesis of 20a was a slight modification of this route, as the amine was acetylated after the Sonogashira reaction and the resulting amide 16 was allylated following the Smith procedure that uses powdered KOH in anhydrous THF with tetrabutylammonium iodide. In this reaction the TMS group is also lost, giving directly the desired enyne 20a in 98% yield (Scheme 6).

All previously prepared substrates were reacted in the presence of ruthenium catalysts 1 and 2. Compound 8b was used as a model to study the best reaction conditions. Temperature, solvent, and catalyst loading were compared using first generation catalyst, and the results are summarized in Table 1. Following these results the selected reaction conditions consisted of using 7% catalyst in refluxing dichloromethane. With regard to catalyst 2, the current thinking is that intermediates coming from this complex are able to complete more turnovers than those derived from 1 although they are formed in less extension. Thus, the amount of catalyst loading would be less important. As the reaction of compound 8b did not complete with catalyst 2 in any of the conditions used, we used 8c. We reacted this compound (entries 8–10) with 3%, 5%, and 7% of catalyst 2 and found similar results. We selected a 5% loading for the rest of reactions. The above selected conditions were used with the rest of substrates (entry 6, Table 1 for catalyst 1 and entry 9 for catalyst 2). Table 2 summarizes the results obtained in these reactions.

Alcohol 7a gave the corresponding diene, which could only be observed in the spectrum of the crude mixture.
This reaction product decomposed after a few hours at room temperature. All attempts to isolate it were unsuccessful. In addition, no reaction was observed with the TBDMS-protected compound 8a with any of the catalysts, probably because of steric hindrance of the substrate. We opted thus to react 7a and protect the hydroxydiene in the crude mixture with a TBDMS group, obtaining 24a with 50% yield after the two reaction steps (Scheme 7).

The rest of the examples selected yielded the desired products with, in general, good yields. The exception was 22, which did not react, probably as a result of interaction with the unprotected amine. The reaction of the two ethers 21 using complex 1 gave only 50% conversion after 2 h, and it was not improved after 18 h. Thus, we added a total of 10% catalyst divided into four equal portions, which were added every 30 min. Before each addition, the reaction mixture was filtered through Celite. With this procedure, the remaining starting material was reduced to less than 10% and we isolated the dienes 29 with good yields. When using catalyst 2 the results were similar with one portion of complex while it was not possible to complete the reaction using partitioned addition of the catalyst. The reaction did not complete when carried out in toluene at 80 °C or at reflux. In this latter case we obtained complex mixtures in the reaction of 21a.

With respect to second-generation catalyst 2, it is possible that this complex is more sensitive to steric hindrance as reactions with 8b, 20a, and 21a,b gave conversions of only 50–65% in the crude 1H NMR spectra. These results were not improved when changing solvents or temperatures or when adding the catalysts in portions. On the other hand, complex 2 improves the results with less hindered substrates such as 7b, 8c, 9, 20b, or 13. The latter substrate yields compound 26, the well-known Dane’s diene.

Some of the substrates shown in Table 2 were also reacted with the Hoveyda–Grubbs catalyst, 3. This complex has the advantage that it can be purified by column chromatography and recovered at the end of the reaction. It is also stable at higher temperatures. We tried to improve results with ethers 21a,b. Metathesis reaction with enynes bearing oxygen are somewhat
reaction completed in 24 h and resulted in a 3:1 mixture.
We used toluene and DCM as solvents, at room tempera-
tion of compound 21.

When designing the type of substrates used for these
studies we had observed that when using compounds in
which the double bond was conjugated with the aromatic
ring, the cyclization did not occur. We used compound
30 to test the previously optimized conditions. Neither
complexes 1 nor 2 were able to catalyze the cyclization.
Starting material was recovered in both cases. On the
other hand, compound 30 reacted with 5% 3 and was
totally converted into 31, which was isolated in 65% yield
(Scheme 8).

Next we addressed the Diels–Alder reaction of some of
these products. As a model we performed the cycliza-
tion of compound 25 with maleic anhydride (Scheme 9).
We used toluene and DCM as solvents, at room temper-
ature, observing in both cases after 3 days a 2:1 mixture
of rac-32 and rac-33. When using refluxing DCM, the
reaction completed in 24 h and resulted in a 3:1 mixture
of the same compounds (71% yield in mixture). The major
adduct, rac-32, was isolated in 50% yield. These com-
 pound s were assigned as the stereoisomers depicted in

![Scheme 8](image)

![Scheme 9](image)

![Scheme 10](image)

![Scheme 11](image)

erratic: there are results in the literature in which this
functionality seems to be beneficial, others in which no
influence is observed, and in the majority of cases, a
negative influence is reported.17 A coordination of the
oxygen with the catalyst is usually claimed as the reason
for this result. In our hands, the reaction of compounds
21 with 5% complex 3 did not complete using DCM as
solvent, even at reflux. Thus we used toluene at 80 °C,
and we were pleased to observe total conversion with both
ethers and a final yield of 72% and 70%, respectively.
This result avoids the partitioned addition of the catalyst.
The same conditions were used with enynes 13 and 20a.
 Whereas the reaction of 13 did not complete after 12 h,
compound 20a gave 70% yield and total conversion, a
worse result than when using catalyst 1 (see entry 8,
Table 2).

We tried the one-pot obtention of these adducts from enynes 20a and 13 by adding the dienophile to the
metathesis reaction mixture, once total conversion of the
enzyme was verified (TLC). Regarding compound rac-34
the yield of the two-step one-pot process was 85%, after
36 h of reaction in refluxing dichloromethane. This result
shows a possible beneficial action of the ruthenium complex in the Diels–Alder reaction (Scheme 10).

Compound rac-35 reached 68% yield, also improving
the two-step procedure. As this latter case is a possible
entry to new estradiol-related compounds, we tried to
improve this result by adding a Lewis acid as cocatalyst.
Scheme 11 shows the results obtained when adding 1
equiv of several Lewis acids jointly with the dienophile.
TiCl4 at low temperature gave the best results (90%).

At this point we thought it was worth trying this
methodology to obtain indoles.21 This would imply the
synthesis of aromatic enamines or ynamines. Both ap-
proaches were addressed. We prepared enamine 36 and
ynamine 37 following our previously reported proce-
dure.22 When reacting these compounds with catalyst 1,
no conversion was detected (TLC) and decomposition of
starting material occurred when the reaction time was
prolonged. Catalyst 2 gave the desired cyclization prod-

1998, 39, 7595. In intermolecular enzyme reactions coordination effects
of oxygen atoms have also been identified sometimes with an accelerat-
Other authors circumvented this problem with adequate choice
(18) Compound 30 was obtained from 2-iodoacetanilide by Still-
reaction with tributylvinyltin and subsequent propargylation of
the amide. See Supporting Information for details.

65, 1697. (b) García Ruano, J. L.; Alemparte, C.; Martín Castro, A.;
(20) This would imply a nonmetathetic behavior of the ruthenium
9, 12358. (21) The only example of indole synthesis using olefin RCM:
Arisawa, M.; Terada, Y.; Nakagawa, M.; Nishida, A. Angew. Chem.
Int. Ed. 2002, 41, 4732. (22) Domínguez, G.; Casarrubios, L.; Rodriguez-Noriega, J.; Pérez-
products when toluene at 80 °C was used.\textsuperscript{11a} Compound 37 gave a complex crude mixture in which N-tosyl-2-vinyllindole was the major product. However, it was impossible to purify it probably as a result of instability of this product in the presence of traces of ruthenium species (Scheme 12).

On the other hand, compound 36 gave a clean conversion into a mixture of the vinyllindole 38 and its dimmer 39. As 38 is not a diene, a partial cross metathesis reaction had occurred after cyclization. When using catalyst 3 in the same conditions, yields improved for both products although there was a similar ratio of both. We were unable to find conditions that would allow the synthesis of only one of these products. When using catalyst 2, high dilution (100 mL/mmol), and short reaction times (2 h) in toluene (80 °C) we reached 60% yield of 38 and 25% yield of 39. With catalyst 3, longer reaction time (18 h) and addition of a further 2% portion of catalyst, we reached 70% yield of 39 and 20% yield of 38 (Scheme 13).

One possible way to obtain only one reaction product would be performing a tandem RCM/Diels–Alder process in which the cycloaddition would be more rapid than the cross metathesis reaction. When carrying out the domino process from 36, using maleic anhydride as dienophile, we observed in the crude a (1:1.5) mixture of rac-40 and rac-41, which could not be separated. On the other hand, with dimethyl acetylenedicarboxylate we were pleased to obtain only compound rac-42 with 65% yield. This latter compound is related with carbazole alkaloids. Additionally, compounds 38 and 39 were separately reacted with maleic anhydride. They gave the corresponding adducts rac-40 and rac-41 in good yields (Chart 2).

To assign the relative configuration of these compounds, a single crystal of rac-40 was submitted to X-ray diffraction analysis. This analysis shows a (3aS*,3bS*,10S*,10aS*) relative stereochemistry for this compound in which all hydrogen atoms present in the stereogenic centers are positioned on the same face. We assume the same relative stereochemistry for compounds rac-41 and rac-42.

From the results we have shown here it is clear that there is not a simple and predictable behavior of the three catalysts used. The claimed greater efficiency of second-generation complexes is true for substituted olefins and nonhindered substrates, whereas complex 1 gives better results with hindered ones. This differences may have their origin in the reaction course, which may be slightly or even completely different from one catalyst to another. To have more information on these reactions, we proceeded to follow some of them by $^1$H NMR. The reactions were carried out with 25% catalyst in a 0.025 M solution of starting material.\textsuperscript{19} We selected as starting materials compounds 20a, 43, and 44. Compound 43 was synthesized to see the influence of substituted olefin fragments in the reaction, and 44 was selected as a parent olefin RCM substrate to check possible differences in the reaction course (Scheme 14).\textsuperscript{23}

We registered a proton spectrum every 5 min during the first hour and every 15 min until total completion or 4 h of reaction. We followed the transformation of the starting material into the final product, the possible appearance of signals corresponding to styrene, and the changes in the signal of the carbene proton of the catalyst. The results are summarized in Table 3. We indicate the initial position of this carbene C–H signal and its eventual changes at the end of the reactions. We also made $^1$H NMR spectra of complexes 1, 2, and 3 in the different solvents used for these reactions. The position of the carbene C–H signal in the spectra of the catalyst alone is also indicated.

When used, the first generation catalyst 1 produces styrene, and its carbenic signal disappears during the reaction (entries 1 and 6), any other carbenic species not being detectable at the end. During the enyne metathesis (entry 1) two new carbenic species are detected, a triplet (J = 4.3 Hz) at 18.28 ppm and a singlet at 20.7 ppm. As
Hoye has reported recently, these signals may correspond with the carbenic species consistent with path a, Scheme 3, supporting that this reaction course is operating with catalyst 1, although other paths may also operate at the same time. With catalyst 2, the ruthenium complex remains apparently unaltered during the whole reaction when using CD$_2$Cl$_2$ or CDCl$_3$ (entries 2, 5, and 7) and is partially transformed into a new complex when using aromatic solvents (entries 3, 8, and 9). In all of these reactions no styrene was detected. This would discard path a and suggests path b is predominant. Finally the carbenic signal of complex 3 diminishes during the first hour (when final product is hardly detected) and reappears after 2 h. A comparative figure of the evolution of the low field signals of the reactions of entries 1, 2, and 4 from Table 3 is shown in Figure 1."}

![Figure 1](image-url)  
**Figure 1.** Comparative evolution of the carbenic signal of catalysts 1, 2 and 3 in the reactions of compound 20a (entries 1, 2, and 4, Table 3).

| entry | substrate | catalyst | solvent | temp | product | time (h) | conversion (%) | $^1$H NMR signal$^a$ | | catalyst | initial | final |
|-------|-----------|----------|---------|------|---------|---------|---------------|----------------------|----------------|---------|---------|
| 1     | 20a       | 1        | CDCl$_3$ | rt   | 27a$^b$ | 3$^c$   | 65            | 19.98                | 19.98       | none |
| 2     | 20a       | 2        | CDCl$_3$ | rt   | 27a$^b$ | 3$^c$   | > 95          | 19.13                | 19.13       | 19.13 |
| 3     | 20a       | 2        | C$_6$D$_6$| rt   | 27a    | 5       | > 95          | 19.63                | 19.62       | 19.62; 18.41 |
| 4     | 20a       | 3        | CDCl$_3$ | rt   | 27a$^b$ | 3$^c$   | 83            | 16.56                | 16.57       | 16.57 |
| 5     | 43        | 2        | CD$_2$Cl$_2$| rt | 45    | 3       | > 95          | 19.07                | 19.07       | 19.07 |
| 6     | 44        | 1        | CDCl$_3$ | rt   | 46$^b$ | 0.5     | > 95          | 19.98                | 19.98       | none |
| 7     | 44        | 2        | CDCl$_3$ | rt   | 46$^b$ | 1       | > 95          | 19.13                | 19.13       | 19.13 |
| 8     | 44        | 2        | Xyl-d$_2$| rt   | 46$^b$ | 5       | > 95          | 19.22                | 19.22       | 19.22; 17.96 |
| 9     | 44        | 2        | C$_6$D$_6$| rt   | 46$^b$ | 6       | > 95          | 19.63                | 19.62       | 18.41 |

$^a$ Position of the carbene C–H signal. $^b$ Styrene was formed in the reaction. $^c$ The reaction was not totally completed. $^d$ Some cross metathesis (dimeric) product is detected.
more turnovers than the intermediate coming from 1. This agrees with the values of the dissociation constants found by Grubbs and would explain that styrene is not detected.\(^{(26)}\) One other possible explanation for this unchanging benzylidene signal would be that this catalyst begins transferring the benzylidene onto the substrate releasing a Ru=CH\(_2\) complex. This methyldiene would react with the alkene to give a vinylcarbene that would ring close with the alkene (a 3-phenylallylamide), regenerating the benzylidene complex 2 in each turnover (Scheme 15).\(^{(25)}\)

The apparent disappearance of the signal of catalyst 3 and its recovery after 1 h of reaction is something consistent with the ability of this complex to regenerate after the reactions. This has been shown in olefin metathesis reactions, and it also occurs in these enyne processes. As proposed by Hoveyda this complex reacts with the olefin (in alkene metathesis), releasing the corresponding styrene derivative. Upon consumption of the reactives, this styrene reacts with the metal carbene complex to regenerate the initial catalyst.\(^{(3)}\) According with our observations similar behavior is assumable with enyne reactions.

On the other hand, Mori has recently reported a new cyclization process catalyzed by ruthenium species in which a ruthenacyclopentene is proposed as intermediate.\(^{(26)}\) Our observations in the reactions with complexes 2 and 3 may indicate that a possible reaction course in which this kind of metallocycles would be formed followed by cyclobutene formation and cyclorreversion may not be completely discarded.\(^{(27)}\) It is clear that more evidence would be necessary, but this reaction course would also explain the behavior of complex 2, which may be recovered after every cycle by recomplexation of the phosphine.

Also in olefin RCM reactions (entries 6 and 7) the same pattern is observed, catalyst 2 remaining unaltered in the reaction, while 1 produces styrene and disappears during the process.

Another interesting aspect of this experiments is the changes observed when switching the solvent to an aromatic one. When using xylene or benzene, new carbonic species are formed. It would be possible that these solvents interact with the metal, forming new complexes that also would be capable of catalyzing the metathesis reaction. No change in the spectrum was observed when heating the catalyst alone in xylene for 2 h at 40 °C. The reactions in aromatic solvents need more time to complete. We are investigating the nature of these species that may resemble the \(\nu^6\) complexes described in the literature,\(^{(28)}\) some of them reported as efficient catalyst for metathesis reactions.\(^{(29)}\)

In conclusion, we have described the use of enynes connected through aromatic rings as substrates for the enyne metathesis reaction that affords quinoline, benzoazepine, chromane, hydronaphthalene, indole, and other polycyclic derivatives. The reactivity of the most popular ruthenium complexes is studied and affords no exact rule for their preferable use, although second generation complexes give better results with monosubstituted defins and worse with hindered substrates. Some polycyclic compounds are obtained in a tandem or stepwise RCM-Diels–Alder process. We have shown here some data on the enyne RCM reaction course. These data support the first complexation of the alkene with the ruthenium as has been proposed by other groups.\(^{(3,26,28)}\) They also point to possible differences in the reaction course when using the different catalysts.

### Experimental Section

**General Procedures for Metathesis Reaction. Method A.** A 1 mmol portion of enyne was dissolved in 20 mL of dry dichloromethane under argon. To this solution was added 0.05–0.07 mmol of Grubbs catalyst (1 or 2), and the reaction was refluxed until completion (TLC). Filtration through Celite, evaporation of the solvent, and purification by column chromatography yielded the corresponding diene.

**Method B.** A 1 mmol portion of enyne was dissolved in 20 mL of dry dichloromethane under argon. To this solution was added 0.10 mmol of catalyst 2, divided into four equal portions, which were added every 30 min, while the mixture was refluxed. Before each addition, the reaction mixture was cooled and filtered through Celite. Evaporation of the solvent and purification by column chromatography yielded the corresponding diene.

**Method C.** A 1 mmol portion of enyne was dissolved in 50 mL of dry toluene under argon. To this solution was added 0.05 mmol of catalyst 3, and the reaction was heated at 80 °C until completion (TLC). Evaporation of the solvent and purification by column chromatography yielded the corresponding diene.

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\(^{(25)}\) We thank one of the referees of this work for useful proposals on these mechanistic aspects.


\(^{(27)}\) These ruthenium metalacycles have been proposed in cyclization catalysed by noncarbene ruthenium(II) species: (a) Trost, B. M.; Toste, F. D. J. Am. Chem. Soc. 2000, 122, 724. (b) Chatani, N.; Kataoka, K.; Murai, S. J. Am. Chem. Soc. 1996, 120, 9104.


13C NMR: 286 mg (1.9 mmol) of DMF and treated with 162 mg (2.4 mmol) of imidazole and resulting mixture was stirred for 2 h. The reaction was quenched with 20 mL of ice- H₂O/ Et₂O (1:1). The organic layer was washed with abundant H₂O, dried over MgSO₄, filtered, and concentrated. Flash chromatography (hexane) afforded 81 mg (50%) of 24a as a yellow solid (mp 97–98 °C (EtAcO)). ¹H NMR: δ: 0.09 (s, 3H), 0.18 (s, 3H), 0.96 (s, 9H), 5.28 (s, 1H), 5.45 (s, 1H), 11.55 (s, 1H), 5.86 (s, 1H), 17.68 (s, 1H), 6.33 (s, 1H), 6.68 (dd, 1H, J = 17.6 Hz, J = 17.1 Hz), 7.18–7.32 (m, 3H), 7.45 (t, 1H, J = 7.1 Hz). ¹³C NMR: δ: 174.0, 143.1, 141.1, 134.3, 130.0, 127.9, 126.1, 123.5, 112.0, 117.6, 76.5, 29.8, 18.3, 4.2. IR (neat): ν: 1630, 1610 cm⁻¹. Anal. Calcd for C₂₄H₂₄O₅Si: C, 74.94; H, 8.89. Found: C, 74.69; H, 8.71.

16. tert-Butyldimethylsiloxyl-5-vinyl-2,3-dihydro-1H-benzocycloheptene (24c). Following method A, from 100 mg (0.33 mmol) of 38 and 34 mg (0.02 mmol) of catalyst 2, 93 mg (93%) of 24c was obtained as a yellow oil. ¹H NMR: δ: 0.00 (s, 3H), 0.18 (s, 3H), 0.96 (s, 9H), 5.28 (s, 1H), 5.45 (s, 1H), 11.55 (s, 1H), 5.86 (s, 1H), 17.68 (s, 1H), 6.33 (s, 1H), 6.68 (dd, 1H, J = 17.6 Hz, J = 17.1 Hz), 7.18–7.32 (m, 3H), 7.45 (t, 1H, J = 7.1 Hz). ¹³C NMR: δ: 174.0, 143.1, 141.1, 134.2, 130.0, 127.9, 126.1, 123.5, 112.0, 117.6, 76.5, 29.8, 18.3, 4.2. IR (neat): ν: 1630, 1610 cm⁻¹. Anal. Calcd for C₂₄H₂₄O₅Si: C, 74.94; H, 8.89. Found: C, 74.69; H, 8.71.

13C NMR: 286 mg (1.9 mmol) of DMF and treated with 162 mg (2.4 mmol) of imidazole and resulting mixture was stirred for 2 h. The reaction was quenched with 20 mL of ice- H₂O/ Et₂O (1:1). The organic layer was washed with abundant H₂O, dried over MgSO₄, filtered, and concentrated. Flash chromatography (hexane) afforded 81 mg (50%) of 24a as a yellow solid (mp 97–98 °C (EtAcO)). ¹H NMR: δ: 0.09 (s, 3H), 0.18 (s, 3H), 0.96 (s, 9H), 5.28 (s, 1H), 5.45 (s, 1H), 11.55 (s, 1H), 5.86 (s, 1H), 17.68 (s, 1H), 6.33 (s, 1H), 6.68 (dd, 1H, J = 17.6 Hz, J = 17.1 Hz), 7.18–7.32 (m, 3H), 7.45 (t, 1H, J = 7.1 Hz). ¹³C NMR: δ: 174.0, 143.1, 141.1, 134.3, 130.0, 127.9, 126.1, 123.5, 112.0, 117.6, 76.5, 29.8, 18.3, 4.2. IR (neat): ν: 1630, 1610 cm⁻¹. Anal. Calcd for C₂₄H₂₄O₅Si: C, 74.94; H, 8.89. Found: C, 74.69; H, 8.71.
a white solid (mp 272–273 °C (EtOAc)). 1H NMR: δ 1.63 (d, 3H, J = 7.1 Hz), 2.54–2.61 (m, 1H), 2.61 (s, 3H), 3.33–3.39 (m, 1H), 4.63–4.69 (m, 1H), 4.89–4.91 (m, 1H), 6.06 (t, 1H, J = 3.8 Hz), 7.06–7.12 (m, 1H), 7.32–7.33 (m, 2H), 7.47 (d, 1H, J = 7.8 Hz). 13C NMR: δ 170.6, 169.0, 168.7, 144.0, 136.5, 130.3, 126.6, 123.6, 121.7, 119.0, 114.3, 59.1, 43.6, 42.1, 32.1, 25.5, 16.6. IR (KBr): ν 1850, 1770, 1640, 1480, 1470 cm⁻¹.

Anal. Calcd for C₁₇H₁₅NO₄: C, 68.68; H, 5.09; N, 4.71. Found: C, 68.72; H, 5.13; N, 4.76.

(3aS*,3bS*,10S*,10aS*)-4-Acetyl-10-(1-acetylindol-3-yl)-3b,4,10,10a-tetrahydro-3aH-furo[3,4-a]carbazole-1,3-dione (rac-41). To a solution of 147 mg (0.43 mmol) of 39 in 20 mL of anhydrous toluene was added 37 mg (0.43 mmol) of maleic anhydride, and the mixture was refluxed for 20 h. The crude was concentrated and purified by flash chromatography (hexane/EtOAc 1:1), and 103 mg (55%) of 41 was obtained as a white solid (mp 261–262 °C (EtOAc)). 1H NMR: δ 2.66 (s, 3H), 2.72 (s, 3H), 3.82–3.87 (m, 1H), 3.95–3.99 (m, 1H), 4.79–4.85 (m, 1H), 5.15–5.17 (m, 1H), 6.55 (t, 1H, J = 3.8 Hz), 7.12–7.18 (m, 1H), 7.34–7.47 (m, 3H), 7.39 (s, 1H), 7.53–7.60 (m, 3H), 8.52 (d, 1H, J = 7.7 Hz). 13C NMR: δ 169.4, 169.1, 168.5, 168.1, 144.2, 138.0, 135.9, 130.9, 126.3, 125.8, 124.0, 123.8, 122.1, 118.6, 117.8, 117.1, 117.1, 115.1, 114.5, 59.4, 43.0, 41.7, 34.2, 25.6, 24.2. IR (KBr): ν 1850, 1780, 1710, 1650, 1450, 1390 cm⁻¹. Anal. Calcd for C₂₆H₂₀N₂O₅: C, 70.90; H, 4.58; N, 6.36. Found: C, 70.55; H, 4.64; N, 6.31.

(3S*,9aR*)-Dimethyl 9-Acetyl-3-methyl-9,9a-dihydro-3H-carbazole-1,2-dicarboxylate (rac-42). To a solution of 200 mg (1.0 mmol) of 36 in 85 mL of anhydrous toluene was added 60 mg (0.07 mmol) of catalyst 2, and the reaction was stirred at room temperature for 3 h. Then 0.12 mL (1.0 mmol) of dimethyl acetylenedicarboxylate was added, and the reaction was refluxed for 12 h. The mixture was concentrated and purified by flash chromatography (hexane/EtOAc 2:1), and 212 mg (65%) of rac-42 was obtained as a white solid (mp 154–155 °C (EtOAc)). 1H NMR: δ 1.38 (d, 3H, J = 7.1 Hz), 2.48 (s, 3H), 3.15–3.27 (m, 1H), 3.74 (s, 3H), 3.78 (s, 3H), 5.13–5.17 (m, 1H), 6.03 (m, 1H), 7.10 (t, 1H, J = 7.7 Hz), 7.27–7.33 (m, 2H), 7.50 (d, 1H, J = 7.7 Hz). 13C NMR: δ 170.2, 168.1, 129.5, 128.1, 123.8, 123.6, 123.3, 121.3, 120.6, 120.3, 115.0, 114.8, 60.4, 52.4, 52.2, 33.7, 25.0, 17.3. IR (KBr): ν 1730, 1670, 1600 cm⁻¹. Anal. Calcd for C₁₉H₁₉NO₅: C, 66.85; H, 5.61; N, 4.10. Found: C, 66.60; H, 5.57; N, 4.03.

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Supporting Information Available: Full characterization of compounds 6a,b,c, 7a,b,c, 8a,b,c, 9, 10–13, 17b, 18, 19, 20b, 21b, 22, 23b, 24b, 25, 27b, 29a, 30, rac-34, and 43–46; ORTEP drawing for rac-40; spectra of reactions described in Table 3; cif file with details on the X-ray analysis of compound rac-40. This material is available free of charge via the Internet at http://pubs.acs.org.

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